Reaction Rates of Hydrogen, Ammonia, and Methane with Mixtures of Atomic and Molecular Oxygen

EDGAR L. WONG AND A. E. POTTER, JR.

Lewis Research Center, National Aeronautics and Space Administration, Cleveland, Ohio

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The stirred-reactor technique was used to measure the reaction rates of H_2, NH_3, and CH_4 with mixtures of atomic and molecular oxygen ($O+O_2$) at temperatures ranging from 350° to 600°K. A mass spectrometer capable of detecting atomic oxygen and hydrogen was used to analyze the reacting mixture in the stirred reactor. It was discovered that atomic oxygen could be quantitatively monitored by the mass spectrometer at a mass-to-charge ratio of 8. The reaction of H_2 with the $O+O_2$ mixture was found to be a chain reaction, with four to six atoms of oxygen consumed for each hydrogen molecule. The rate constant for the disappearance of atomic oxygen was $3\times10^{13}\exp(-8300/RT)$ cc $mole^{-1}$ sec^{-1}. The products of the reaction were H_2O and H. The reactions of NH_3 and CH_4 with the $O+O_2$ mixture were complex chain reactions, with a minimum of eight atoms of oxygen disappearing for each molecule of NH_3 or CH_4. Rate constants for atomic-oxygen disappearance were

$$3\times10^{12}\exp(-4800/RT) \text{ cc mole}^{-1}\text{ sec}^{-1} \quad \text{and} \quad 2\times10^{13}\exp(-6900/RT) \text{ cc mole}^{-1}\text{ sec}^{-1},$$

respectively. The products of the former reaction were NO, H_2O, and small amounts of H_2 and H. The products of the latter reaction were H_2O, CO_2, and small amounts of CO, H_2, and H.

INTRODUCTION

REACTIONS of atomic oxygen are important in combustion; however, molecular oxygen is normally present in addition to atomic oxygen. Therefore, kinetic measurements of the reactions of H_2, CH_4, and NH_3 with mixtures of atomic and molecular oxygen ($O+O_2$) at temperatures ranging from 350° to 600°K were undertaken in order to get rate constants and to understand the reaction mechanisms. The reaction of H_2 with $O+O_2$ mixtures has been studied before,[1,2] but not in as much detail as reported herein. The reaction of NH_3 with $O+O_2$ mixtures has recently been studied,[3] but over a smaller temperature range. The rate of the reaction of CH_4 with $O+O_2$ mixtures seems not to have been studied at all.

EXPERIMENTAL

The 300-cc stirred reactor[4] and its connection to the Bendix time-of-flight mass spectrometer is diagrammed in Fig. 1. The reactor and its inlet tubes may be heated to any desired temperature up to 600°K if insulated electrical heating tape is wrapped around them.

The flow of molecular oxygen into the reactor was metered by a small Matheson flowmeter. Flow rates ranged from 1.4 to 1.5 cc/sec (NTP), which yielded pressures in the reactor near 0.8 mm Hg. Reactant gases were metered by observing the rate of pressure decrease in a reservoir of known volume as the gas flowed out of it. A mercury manometer was used to follow the pressure changes in the reservoir for all gases except NO_2, for which a stainless-steel Wallace–Tiernan Bourdon-type gauge was necessary.

For the aforementioned experimental conditions [300-cc stirred reactor, 1.5 cc/sec (NTP) flow at pressure of about 1 mm Hg], the requirement for an efficient stirred reactor was satisfied.[4] The ratio of residence time to diffusion time was about 10.

The purity and sources of various gases used in this study are described in Table I.

Atomic oxygen was generated in flowing molecular oxygen by a microwave discharge from a Raytheon Model KV 104(NB) 100-W microwave generator. In order to maximize the production of oxygen atoms, the standard antenna accompanying the equipment was replaced by a Raytheon tapered waveguide section (Part No. 7097–1001). The concentration of atomic oxygen normally produced was about 20% at pressures near 1 mm Hg, as determined by the standard technique of titration with NO_2.[1] It is thought that traces of moisture in the O_2 may have been responsible for the high yield of atomic oxygen, although no H_2O or H was detectable, mass spectrographically, in the gas. Wall recombination of atomic oxygen was minimized by rinsing out the apparatus with 20% phosphoric acid.

Mass Spectrometry

In order to find rate constants from the stirred reactor, it is necessary to measure the concentrations of both the reactant gas and atomic oxygen. For this purpose, a Bendix Model 14–101 time-of-flight mass spectrometer was attached to the exit of the stirred reactor. Analysis of the stable species with the mass spectrometer presents no problem, but analysis for

[1] F. Kaufman, *Progress in Reaction Kinetics* (Pergamon Press, Ltd., London, 1961), pp. 1–40.
[2] P. Harteck and U. Kopsch, Z. Physik. Chem. **B12**, 327 (1931).
[3] I. I. Avramenko, R. V. Kolesnikova, and N. L. Kuznetsova, Izv. Akad. Nauk S.S.S.R. Otd. Khim. Nauk. **6**, 983 (1962).
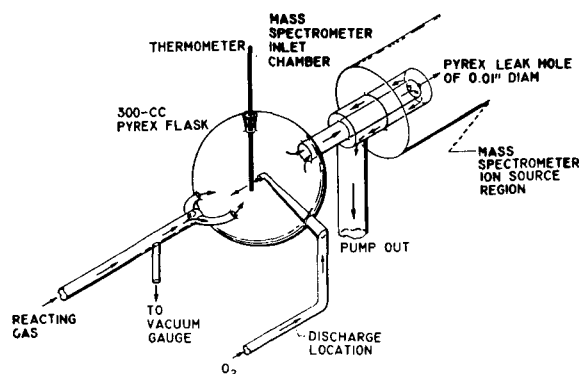[4] G. B. Kistiakowsky and G. G. Volpi, J. Chem. Phys. **27**, 1141 (1957).

FIG. 1. Stirred reactor and connection to mass spectrometer.

atomic oxygen is more difficult. To minimize atom recombination in the vicinity of the leak into the mass spectrometer, a leak hole with a diameter of about 0.01 in. was formed in a thin sheet of Pyrex glass. The ionizing electron beam is located about 1 mm from the leak for this model of time-of-flight mass spectrometer. With this arrangement, it was found that atomic oxygen was detectable at a mass-to-charge ratio (m/e) of 16, but quantitative interpretation was difficult due to strong interference from molecular oxygen, which was always present. However, it was found that atomic oxygen could be monitored at $m/e=8$, or O^{++} with an ionizing electron voltage of 80 to 85 V since in this region of the mass spectrum there is negligible background interference. Using these higher electron voltages resulted in relative ion currents for the O^{++}, O^{+}, and O_2^{+} peaks of 0.004, 1.0, and 8.0, respectively, for about a 20% atomic concentration.

It was found that, at constant pressure, the ion current at $m/e=8$ was directly proportional to the atomic-oxygen concentration. For this test, atomic-oxygen concentration was varied at constant pressure by changing the power setting on the microwave generator. The atomic-oxygen concentration was measured by NO_2 titration.

The ion current at $m/e=8$ for constant O_2 flow rates and discharge power settings decreased with increasing pressure. This was observed by adding inert gases such as argon or nitrogen to the stirred reactor. Three effects can contribute to this decrease; these are: decrease in efficiency of the discharge, recombination in the stirred reactor, and recombination or sensitivity changes in the ion source.

The effect of pressure on the discharge efficiency was measured by NO_2 titration and found to be small. When the pressure was doubled, the total number of O atoms was reduced by 10%. Consequently, for pressure increases of up to 30%, changes in the discharge efficiency were neglected. The effect of recombination in the stirred reactor may be approximately taken into account by assuming that the major processes of recombination are $O+O_2+M \rightarrow O_3+M$, $O+O+M \rightarrow O_2+$
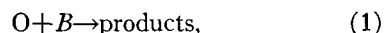
M, and $O+O_3 \rightarrow 2O_2$. Subtracting the decrease expected from these processes from the observed decrease gives the decrease due to sensitivity changes in the ion source. These results were used in the reaction-rate measurements to correct the observed ion currents at $m/e=8$ for the effects of pressure changes after calibration.

Calibration of the mass spectrometer for atomic oxygen was done before (and occasionally after) each run by titration with NO_2 to determine the atomic-oxygen concentration corresponding to a given peak height.

As to analysis of the reaction products, the mass spectrometer served to give qualitative results: that is, it indicated what species were present and what were not. The ability of the mass spectrometer to detect unstable species proved especially valuable in analysis of the products, since it proved possible to detect atomic hydrogen as a product species.

Calculation of Rate Constants

Calculation of rate constants in the stirred reactor for atomic-oxygen reactions is complicated by atom recombination. Suppose a gas B, which reacts with atomic oxygen by a bimolecular process, is added. The following reactions occur in the stirred reactor:

$$O+B \rightarrow \text{products}, \qquad (1)$$

$$O+O_2+M \rightarrow O_3+M, \qquad (2)$$

$$O+O_3 \rightarrow 2O_2, \qquad (3)$$

$$O+O+M \rightarrow O_2+M, \qquad (4)$$

$$O+\text{surface} \rightarrow \tfrac{1}{2}O_2. \qquad (5)$$

Under the conditions of our experiment ($\sim 20\%$ atomic oxygen, phosphoric-acid-coated walls), Reaction (5) contributes little to the loss of atomic oxygen in the stirred reactor and is neglected. Since the steady state for ozone in the reactor is assumed, then the rate of disappearance of atomic oxygen by Reaction (3) equals that by Reaction (2). The total rate is therefore

$$\frac{d[O]_t}{dt} = \frac{d[O]_B}{dt} + \frac{2d[O]_2}{dt} + \frac{d[O]_4}{dt}, \qquad (6)$$

where the subscript meanings are t for total, B for reaction with B, 2 for Reaction (2), and 4 for Reaction (4). Expressing the rates of Reactions (1), (2),

TABLE I. Purities and sources of gases.

Gas	Percent purity	Source
Oxygen	99.5	Burdette Co.
Methane	99 (cp grade)	Matheson Co.
NO_2	99.5	
H_2	99.9 (prepurified)	
NH_3	99.9 (anhydrous)	

and (4) in terms of rate constants, and the differential on the left side of Eq. (6) as a finite difference appropriate to the stirred reactor, results in

$$([O]^0-[O])/t = +k_1[O][B]+2k_2[O][O_2][M]$$
$$+k_4[O]^2[M], \quad (7)$$

where $[O]^0$ is the concentration of atomic oxygen in the complete absence of chemical reaction, and $[O]$ is the actual concentration with chemical reactions. The quantity $[O]^0$ was determined by titration with NO_2 in the stirred reactor. The reaction of NO_2 with O is so fast that it completely outstrips the recombination reactions. Consequently, titration with NO_2 yields the concentration $[O]^0$. The concentration $[O]$ was measured by the mass spectrometer, as discussed above. The concentration of B was also monitored by the mass spectrometer. The rate constants k_2 and k_4 were taken as 0.7×10^{14} cc² mole⁻² sec⁻¹ and 1.1×10^{15} cc² mole⁻² sec⁻¹, respectively.[1] The concentration of O_2 and M can be calculated from the concentration $[O]^0$, the flow rates, and the total pressure, which was measured with a McLeod gauge. All quantities required to calculate k_1 (the rate constant for disappearance of atomic oxygen by reaction with B) from Eq. (7) are then known. In practice, the procedure consisted of establishing a flow of atomic and molecular oxygen in the stirred reactor and then simultaneously determining $[O]^0$ and calibrating the mass spectrometer by NO_2 titration. Next, the reactant gas was added to the stirred reactor in a stepwise fashion, measuring $[O]$ with the mass spectrometer after each step. The concentration of the reactant gas in the stirred reactor was measured at only a few of the steps. Concentrations at intermediate steps were determined by interpolation. The results were used with Eq. (7) to calculate a value of k_1 at each step. In this way, a number of rate constants were measured at each temperature.

Limits of Measurement

It was noticed that for very large amounts of the added gas B and for very slow reactions of B with O, the data showed both large scatter and pronounced trends. The reasons for this are twofold. First, for large amounts of the added gas B, the pressure correction to the ion current becomes large. Second, for very slow reactions of B with O, the correction term for oxygen recombination in Eq. (7) becomes large. In both cases, errors in the correction factors can cause large errors in the calculated rate constants. Consequently, an arbitrary limit of 15% was set for the correction factors. All data for which the individual corrections exceeded 15% of $[O]^0-[O]$ were rejected. The remaining data showed much less scatter and no pronounced trends. In terms of experimental variables, this criterion meant that data for which the added gas B increased the pressure in the stirred reactor more than 30%, and that data for which the rate constant

FIG. 2. Rate constants for O-atom disappearance by reaction with H₂.
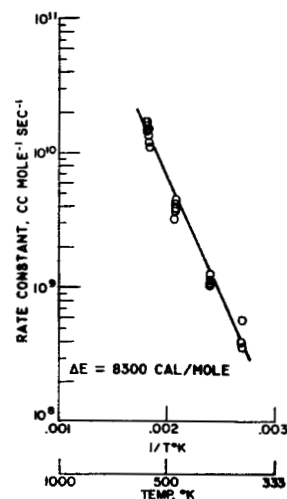
for the reaction of O with B was less than 3×10^8 cc mole⁻¹ sec⁻¹ were all rejected.

Precision and Accuracy

The precision of the data was low, with an average deviation for all the rate constants of about ±20%. Instability of the mass spectrometer was thought to be the major cause of the low precision. The instability appeared to be random, so that large numbers of measurements were made in an attempt to overcome this source of error. The accuracy of the rate constants was estimated to be about ±50%, based on a ±10% possible error in concentration measurement, and a ±1% possible error in temperature measurement. This leads to an accuracy for the activation energies of about ±20%, corresponding to about ±1.5 kcal/mole for the reactions studied.

The errors given for the rate constants in later sections are based on the error estimates given here.

REACTION OF HYDROGEN WITH ATOMIC AND MOLECULAR OXYGEN MIXTURES

The atomic-oxygen concentration was measured in the stirred reactor for different amounts of added hydrogen and at several different temperatures, and the results are presented in Table II. These measurements were used to calculate rate constants for oxygen-atom disappearance according to Eq. (7) where $B=H_2$. A plot of the rate constant against $1/T$ is shown in Fig. 2. The equation of the least-squares line through the data is

$$k=3\pm1.5\times10^{13}\exp(-8300\pm1500/RT)$$

$$\text{cc mole}^{-1}\text{ sec}^{-1}. \quad (8)$$

The activation energy of 8.3 kcal may be compared with the value of 6 kcal estimated by Harteck and Kopsch.[2] The extrapolated rate constant at 295°K is $2\pm1\times10^7$ cc mole⁻¹ sec⁻¹, which agrees well with the

TABLE II. Stirred-reactor measurements of atomic oxygen reaction with H_2, NH_3, and CH_4.

Added gas	Added gas flow (NTP) (cc/sec)	Temperature, (°K)	O_2 flow into discharge (NTP) (cc/sec)	O-atom flow out of discharge into reactor (NTP) (cc/sec)	Total O-atom consumed in reactor (NTP) (cc/sec)	O-atom consumed in reactor due to reaction with added gas (NTP) (cc/sec)	Average fraction of added gas flow consumed in reactor	Pressure (mm Hg)	Residence time (sec)	Rate constant (cc mole⁻¹ sec⁻¹)
H_2	0.254	371	1.37	0.284	0.111	0.099	0.12	0.97	0.178	5.68×10^{8}
	0.390	372	1.37	0.284	0.109	0.096	0.12	1.04	0.178	3.56
	0.480	373	1.37	0.284	0.126	0.115	0.12	1.08	0.176	3.94
H_2	0.343	416	1.43	0.372	0.187	0.178	0.18	1.01	0.150	1.10×10^{9}
	0.106	417	1.43	0.372	0.097	0.083	0.18	0.89	0.150	1.11
	0.381	417	1.43	0.372	0.187	0.178	0.18	1.03	0.149	1.00
	0.259	416	1.43	0.372	0.171	0.162	0.18	0.96	0.149	1.24
H_2	0.088	479	1.43	0.348	0.133	0.127	0.26	0.88	0.131	3.90×10^{9}
	0.353	479	1.43	0.348	0.244	0.241	0.26	1.01	0.130	3.83
	0.082	479	1.43	0.348	0.138	0.132	0.26	0.88	0.131	4.39
	0.353	481	1.43	0.348	0.250	0.248	0.26	1.01	0.130	4.27
	0.075	481	1.43	0.348	0.132	0.126	0.26	0.87	0.130	4.52
	0.325	482	1.43	0.348	0.222	0.219	0.26	0.98	0.129	3.20
H_2	0.067	546	1.43	0.326	0.174	0.171	0.35	0.90	0.119	1.35×10^{10}
	0.092	549	1.43	0.326	0.210	0.208	0.35	0.90	0.118	1.60
	0.034	546	1.43	0.326	0.122	0.118	0.35	0.89	0.121	1.32
	0.086	549	1.43	0.326	0.201	0.199	0.35	0.90	0.117	1.55
	0.141	550	1.43	0.326	0.243	0.242	0.35	0.93	0.118	1.71
	0.046	546	1.43	0.326	0.137	0.133	0.35	0.89	0.120	1.21
	0.047	544	1.43	0.326	0.131	0.127	0.35	0.89	0.120	1.10
	0.100	549	1.43	0.326	0.208	0.206	0.35	0.90	0.117	1.46
	0.174	550	1.43	0.326	0.257	0.256	0.35	0.96	0.119	1.73
CH_4	0.054	353	1.53	0.290	0.093	0.080	0.10	0.86	0.170	2.09×10^{9}
	0.193	354	1.53	0.290	0.140	0.130	0.10	0.94	0.172	1.19
	0.229	356	1.53	0.290	0.146	0.137	0.10	0.96	0.171	1.12
	0.175	354	1.53	0.290	0.110	0.098	0.10	0.92	0.170	0.84
	0.129	355	1.53	0.290	0.112	0.101	0.10	0.90	0.170	1.21
CH_4	0.082	406	1.53	0.290	0.128	0.122	0.18	0.88	0.149	3.67×10^{9}
	0.353	410	1.53	0.290	0.191	0.187	0.19	1.01	0.147	2.23
	0.096	412	1.53	0.290	0.109	0.102	0.19	0.88	0.146	2.48
	0.239	415	1.53	0.290	0.192	0.189	0.20	0.96	0.146	3.45
	0.050	415	1.53	0.290	0.105	0.098	0.20	0.86	0.145	4.54
CH_4	0.154	419	1.53	0.290	0.154	0.150	0.21	0.91	0.143	3.22×10^{9}
	0.440	422	1.53	0.290	0.222	0.200	0.21	1.05	0.142	2.38
	0.045	418	1.53	0.290	0.128	0.122	0.21	0.85	0.143	7.45
	0.243	421	1.53	0.290	0.236	0.234	0.21	0.96	0.144	7.95
	0.051	420	1.53	0.290	0.132	0.126	0.21	0.86	0.143	7.03
	0.210	423	1.53	0.290	0.236	0.235	0.21	0.94	0.143	9.53
	0.052	423	1.53	0.290	0.137	0.132	0.21	0.86	0.142	7.58
	0.123	425	1.53	0.290	0.199	0.196	0.21	0.89	0.142	8.31
	0.293	426	1.53	0.290	0.249	0.248	0.21	0.98	0.141	9.77

TABLE II (*Continued*)

Added gas	Added gas flow (NTP) (cc/sec)	Temperature (°K)	O₂ flow into discharge (NTP) (cc/sec)	O-atom flow out of discharge into reactor (NTP) (cc/sec)	Total O-atom consumed in reactor (NTP) (cc/sec)	O-atom consumed in reactor due to reaction with added gas (NTP) (cc/sec)	Average fraction of added gas flow consumed in reactor	Pressure (mm Hg)	Residence time (sec)	Rate constant (cc mole⁻¹ sec⁻¹)
CH₄	0.033	482	1.45	0.284	0.153	0.150	0.31	0.82	0.127	2.16×10^{10}
	0.019	483	1.45	0.284	0.083	0.078	0.31	0.81	0.126	1.41
	0.094	485	1.45	0.284	0.159	0.157	0.32	0.84	0.124	0.95
	0.088	485	1.45	0.284	0.159	0.157	0.32	0.84	0.125	1.02
CH₄	0.028	534	1.45	0.308	0.116	0.113	0.40	0.82	0.114	2.00×10^{10}
	0.104	537	1.45	0.308	0.199	0.197	0.40	0.86	0.113	1.67
	0.049	537	1.45	0.308	0.161	0.159	0.40	0.82	0.112	2.20
	0.057	538	1.45	0.308	0.182	0.180	0.40	0.83	0.112	2.47
	0.027	537	1.45	0.308	0.128	0.125	0.40	0.82	0.113	2.46
CH₄	0.034	578	1.45	0.308	0.162	0.160	0.47	0.82	0.105	4.16×10^{10}
	0.032	578	1.45	0.308	0.165	0.163	0.47	0.82	0.105	4.51
	0.029	579	1.45	0.308	0.165	0.163	0.47	0.82	0.105	5.07
	0.027	580	1.45	0.308	0.152	0.150	0.47	0.82	0.105	4.52
	0.026	580	1.45	0.308	0.155	0.153	0.47	0.82	0.105	4.93
	0.022	580	1.45	0.308	0.153	0.151	0.47	0.82	0.105	5.75
	0.023	580	1.45	0.308	0.149	0.147	0.47	0.82	0.105	5.08
	0.042	580	1.45	0.308	0.212	0.211	0.47	0.82	0.104	6.91
	0.039	580	1.45	0.308	0.212	0.211	0.47	0.82	0.104	7.34
NH₃	0.127	340	1.44	0.362	0.229	0.221	0.02	0.89	0.181	2.89×10^{9}
	0.142	343	1.44	0.362	0.242	0.235	0.02	0.90	0.180	3.10
	0.034	343	1.44	0.362	0.137	0.120	0.02	0.84	0.180	3.51
	0.100	343	1.44	0.362	0.233	0.225	0.02	0.89	0.182	3.81
	0.101	344	1.44	0.362	0.239	0.231	0.03	0.89	0.182	4.11
	0.034	340	1.44	0.362	0.128	0.110	0.02	0.84	0.180	3.08
	0.091	342	1.44	0.362	0.203	0.192	0.02	0.89	0.184	2.83
	0.088	343	1.44	0.362	0.203	0.192	0.02	0.89	0.183	2.95
	0.088	340	1.44	0.362	0.165	0.149	0.02	0.89	0.185	1.80
	0.163	343	1.44	0.362	0.259	0.253	0.02	0.91	0.180	3.40
	0.151	344	1.44	0.362	0.259	0.253	0.03	0.91	0.180	3.67
NH₃	0.081	424	1.44	0.380	0.244	0.239	0.24	0.89	0.148	0.95×10^{10}
	0.069	427	1.44	0.380	0.254	0.250	0.24	0.88	0.147	1.29
	0.077	427	1.44	0.380	0.257	0.253	0.24	0.88	0.146	1.31
	0.043	426	1.44	0.380	0.194	0.187	0.24	0.86	0.146	1.04
	0.049	427	1.44	0.380	0.194	0.187	0.24	0.85	0.143	0.96
	0.045	427	1.44	0.380	0.194	0.187	0.24	0.85	0.144	1.04
	0.047	425	1.44	0.380	0.192	0.185	0.24	0.86	0.146	0.94
	0.118	430	1.44	0.380	0.278	0.275	0.25	0.90	0.145	1.07
	0.092	428	1.44	0.380	0.260	0.256	0.25	0.90	0.148	1.03
	0.104	429	1.44	0.380	0.259	0.255	0.25	0.90	0.146	0.92
	0.098	430	1.44	0.380	0.260	0.256	0.25	0.90	0.146	0.99
NH₃	0.047	487	1.44	0.381	0.218	0.214	0.40	0.86	0.127	2.10×10^{10}
	0.065	495	1.44	0.381	0.260	0.257	0.42	0.88	0.127	2.57
	0.071	496	1.44	0.381	0.266	0.264	0.42	0.89	0.127	2.56

Water and atomic hydrogen were the only reaction products that could be found. It is felt that the experimental data are not of sufficient precision and completeness to allow formulation of a mechanism for the chain reaction. However, it seems likely that atomic hydrogen is a result of the reaction between OH and O, and that O_2 becomes involved in the chain reaction by the reaction $H+O_2+M \rightarrow HO_2+M$. The most probable reaction for the formation of water is thought to be the reaction of OH with H_2.

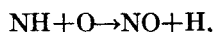## REACTION OF AMMONIA WITH ATOMIC AND MOLECULAR OXYGEN MIXTURES

The over-all rate constant for the disappearance of atomic oxygen by reaction with ammonia was calculated from stirred reactor measurements (Table II). The results are shown in Fig. 4. The equation of the least-squares line through the data is

$$k=3\pm1.5\times10^{12}\exp(-4800\pm1500/RT)$$

$$\text{cc mole}^{-1}\text{ sec}^{-1}. \quad (9)$$

Recently Avramenko, Kolesnikova, and Kuznetsova[3] have reported rate data for this reaction. They made four measurements in the range of 348° to 458°K that show no temperature dependence. A comparison of their data with the data of this report is shown in Fig. 4. The lack of temperature dependence reported by these workers is possibly the result of insufficient temperature range and precision.

The reaction is a chain reaction, as proved by the relative stoichiometry of the reaction. This is shown in Fig. 3, where the number of moles of atomic oxygen consumed per mole of ammonia consumed is plotted against temperature. The ratio is larger than for hydrogen and is a minimum of about 8 in the range 400° to 550°K.

Mass spectrometric analysis of the reaction products showed the main products to be water and nitric oxide. Traces of molecular and atomic hydrogen also were found. Atomic hydrogen probably results from the reaction of OH with O and possibly also from the reaction

$$NH+O \rightarrow NO+H,$$

which could account for the appearance of NO as the only nitrogen-containing product of the reaction. Molecular hydrogen could be formed by the reaction of atomic hydrogen with ammonia. This reaction is more complex than the H_2+O+O_2 reaction.

FIG. 5. Rate constants for O-atom disappearance by reaction with CH₄.
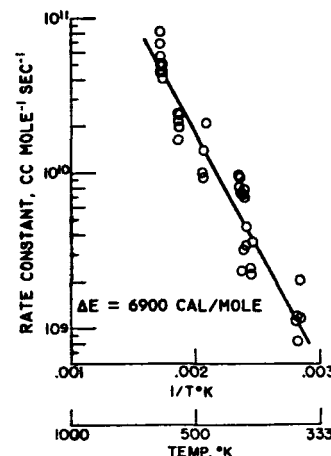
REACTION OF METHANE WITH ATOMIC AND MOLECULAR OXYGEN MIXTURES

Rate constants for the disappearance of atomic oxygen by reaction with methane were calculated from stirred-reactor measurements (Table II) as before. The resulting rate constants are shown in Fig. 5. The equation of the least-squares line through the data is

$$k=2\pm1\times10^{12}\exp(-6900\pm1500/RT)$$

$$\text{cc mole}^{-1}\text{ sec}^{-1}. \quad (10)$$

The activation energy of 6.9 kcal/mole agrees approximately with the values estimated by Geib[5] of 7 kcal/mole and by Steacie and Parlee[6] of 8 kcal/mole.

As in the preceding cases of hydrogen and ammonia, the reaction is a chain reaction. The relative stoichiometry of the reaction is shown in Fig. 3, where the number of moles of atomic oxygen consumed per mole of methane is plotted against temperature. The ratio is a minimum of about 8 in the range of 350° to 500°K.

Mass-spectrometric analysis of the products showed CO_2 and water as the major products, with smaller amounts of CO, traces of H_2, and possibly a trace of H.

It is strange that CO_2 is a major oxidation product. One would expect CO to be formed first, and it is known that CO is oxidized quite slowly by atomic oxygen, so that CO might be expected to be the major carbon-containing product, rather than CO_2. This reaction is evidently the most complex of the three studied.

[5] K. H. Geib, Ergeb. Exakt. Naturw. 15, 44 (1936).
[6] E. W. R. Steacie and N. A. D. Parlee, Can. J. Res. B16, 203 (1938).